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National Water Quality Laboratory
P.O. Box 25585
Denver, CO 80225-0585

NATIONAL WATER QUALITY LABORATORY
TECHNICAL MEMORANDUM 16.01

Subject: Validation of a Radiometer Analytical 870 Titrator and SAC 950 sample changer for alkalinity and acid-neutralizing capacity measurements

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Author(s): Dana Erickson, Analytical Services Nutrients Unit, derickson@usgs.gov, 303-236-3939
Teresa L. Kirschling, Analytical Services Nutrients Unit, tkirschling@usgs.gov, 303-236-3177

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1 INTRODUCTION

A replacement automated titration instrument, a Radiometer Analytical TIM870 with SAC950 sample changer, was installed in December 2015 at the National Water Quality Laboratory (NWQL) eventually to replace the current titration system, a Radiometer TIM860 with SAC90 sample changer. The existing titrator's autosampler is obsolete and may not be repairable if it were to fail. The source method, NWQL laboratory codes, and NWIS method and parameter codes will remain the same (see table 1). A validation study was completed to assess the performance of the replacement instrumentation prior to putting it into production. This report demonstrates equivalence between the existing instrument and its replacement.

Alkalinity and acid-neutralizing capacity (ANC) are measured using the same titration technique. Total alkalinity or ANC refers to NWQL laboratory code (LC) 70 and the use of raw, untreated (RU) samples, and dissolved alkalinity refers to LC 2109 and the use of filtered, untreated (FU) samples.

This method measures the alkalinity of all water types using an automated titration system that employs a combination electrode with pH-sensitive glass membrane. The combination electrode measures the sample pH continually as the automated titration system introduces standard acid titrant into the sample. The acid titrant is approximately 0.01639 normality (N) sulfuric acid in water. The titrant is added in increments until the designated endpoint of pH 4.5 is reached. The titration rate is variable and optimized to operate at the highest feasible speed that can provide accurate analytical results. The titration rate slows as the pH of the sample approaches the endpoint and stops as the endpoint (pH 4.5) is reached. Once the pH has been stable at or below pH 4.5 for 1 minute, the measurement is recorded. Results are expressed as milligram per liter as calcium carbonate (mg/L as $CaCO_3$).

Table 1. Method and analyte parameters with current detection limits.

[mg/L, milligram per liter; $CaCO_3$, calcium carbonate; DLBLK, detection limit by blank data]

Analyte	Laboratory code	Parameter	Method code	Source method[1]	Detection limit (mg/L as $CaCO_3$)	Report type
Alkalinity	2109	29801	TT040	TWRI B5-A1/89	4.0	DLBLK
Acid-neutralizing capacity (ANC)	70	90410	TT040	TWRI B5-A1/89	4.0	DLBLK

[1]Fishman and Friedman (1989)

1.1 Anticipated analytical requirements

During Water Year 2014, 4,324 samples were analyzed for alkalinity and 1,943 samples for ANC. During Water Year 2015, 4,047 samples were analyzed for alkalinity and 1,616 samples were analyzed for ANC. Alkalinity values ranged from 4–1,809 mg/L as $CaCO_3$ and ANC ranged from 4–1,477 mg/L as $CaCO_3$, with 75 percent of samples falling between 4 and 200 mg/L as $CaCO_3$.

1.2 Instrument overview

The current analytical platform is a Radiometer Analytical TIM860 Titration Manager and a SAC90 sample changer. The replacement system is a Radiometer Analytical TIM870 Titration Manager coupled to a SAC950 sample changer. Both systems use the same Ag/AgCl pH electrode: Radiometer combined pH electrode C2701-8. Both systems have a temperature probe and compensate for temperature. Both systems share the same computer and use the same software: TM85. The identical titration method and titrant are used on both instruments. Refer to table 2 for platform information.

Table 2. Basic instrument platform information.

[mL, milliliter]

Instrument	Sampler	pH probe	Approximate sample volume (mL)
Radiometer TIM860	SAC90	Radiometer pH C2701-8	60
Radiometer TIM870	SAC950	Radiometer pH C2701-8	60

2 METHOD

Data collection and statistical analyses for validation studies were conducted over 8 weeks to assess the performance of the replacement instrument. Bias and variability were determined using replicate measurements of quality control samples, blanks (deionized and ASTM Type I water), and representative blended surface and groundwater samples. These blanks and quality control samples were interspersed with environmental samples over the course of five runs. The alkalinity or ANC of 75 environmental samples (approximately 1 percent of annual sample load) was determined on both systems (see attachment 1 for a list of these environmental samples) to identify any bias present in sample measurements relative to the current instrumentation. Environmental samples were randomly selected from available samples logged in at the NWQL. Each selected sample had enough volume to be analyzed on both platforms. Samples were analyzed on both instruments on the same day. Measured environmental sample alkalinities ranged from below the detection limit (4.0 mg/L) to 450 mg/L as $CaCO_3$. The calibrants used in the study for pH were the same for both instruments.

A rinsing test was performed on the replacement Radiometer instrument prior to initiating validation studies. The Radiometer SAC90 rinses the pH electrode by dipping the probe in a rinse cup. The replacement SAC 950 has a dynamic spray rinse feature for rinsing the pH electrode between samples. Standards with alkalinities up to 1,700 mg/L as $CaCO_3$ and samples with conductivities up to 11,800 microsiemens per centimeter (µS/cm) followed by blanks were used to determine if washout times were sufficient to prevent carryover (attachment 2). No carryover was observed for alkalinity or ANC measurements.

The current NWQL detection limit for alkalinity and ANC of 4.0 mg/L was verified using the U.S. Environmental Protection Agency (EPA) procedure (unchanged since 1986; U.S. Environmental Protection Agency, 1986) for the determination of the method detection limit (MDL) (table 3). A 5.0 mg/L alkalinity standard was used as the MDL solution. Seven measurements of this standard were taken, interspersed with samples, in three runs over a period of 2.5 weeks. The MDL was calculated using the equation:

$$MDL = t_{(N-1,1-\alpha+0.99)} \bullet S$$

where t is the Student's t value at the 99 percent confidence level with n-1 degrees of freedom and S is the standard deviation of the replicate analyses.

An assessment of bias and variability for certified reference materials was conducted. Certified reference material alkalinity standards (as mg/L $CaCO_3$) were purchased from Sigma Aldrich at concentrations of 500 and 1,000 mg/L. These standards were diluted to create standards at 5 mg/L for the MDL study, 10 mg/L, and 100 mg/L. A standard reference sample (M-216) was obtained from the U.S. Geological Survey Branch of Quality Systems. A third-party check (TPC) at a concentration of 36.45 mg/L as $CaCO_3$ was purchased from ERA (Golden, Colo.).

Blended groundwater and surface water samples were used to determine the variability of alkalinity and ANC measurements with environmental samples. Four sample waters were prepared by blending several samples of known alkalinity and ANC to fit in the upper and lower one-third of the alkalinity and ANC concentration range of samples analyzed for both groundwater and surface water. These blended sample waters were prepared from older environmental samples already at the NWQL that had been analyzed and were past disposal dates. These various blended waters were analyzed interspersed with environmental samples. Forty-six measurements were made on four separate runs over 8 weeks.

3 RESULTS AND DISCUSSION

3.1 EPA method detection limit study for alkalinity and acid-neutralizing capacity (ANC)

The calculated EPA MDL is 1.44 mg/L as $CaCO_3$ (n=7). Based on historical blank measurements, the NWQL detection limit will remain as 4.0 mg/L for both alkalinity and ANC. The NWQL detection limit will be re-evaluated after the new instrument has been in operation for a year. Table 3 contains the seven individual measurements and the determined EPA MDL.

Table 3: Determination of EPA method detection limit using a 5.0 mg/L $CaCO_3$ solution.

[mg/L, milligram per liter; $CaCO_3$, calcium carbonate; MDL, method detection limit]

Sample	Alkalinity (mg/L as $CaCO_3$)
MDL 1	7.64
MDL 2	6.82
MDL 3	6.54
MDL 4	6.42
MDL 5	6.32
MDL 6	6.46
MDL 7	6.44
Mean	6.66
Standard deviation	0.46
EPA method detection limit	1.44
NWQL detection limit	4.0

3.2 Bias and variability of repeated alkalinity and acid-neutralizing capacity (ANC) measurements of standards and standard reference samples

Bias and variability were assessed for certified reference material standards (table 4). For a 500 mg/L standard, a negative 0.4 percent bias was observed with a variability of 1.0 percent relative standard deviation (RSD). For a 100 mg/L standard, a positive 0.5 percent bias was observed with a variability of 1.7 percent RSD. Comparable bias and variability were shown on the existing TIM860 during the same time frame although the replacement instrument had a measured mean closer to the expected alkalinity value for all three concentrations of certified reference materials.

For standards below 20 mg/L, low variability, but high biases were shown. For a 10 mg/L standard, a positive bias of 16 percent was observed with variability of 1.9 percent RSD. For a 5 mg/L standard analyzed for the MDL study, a positive bias of 33 percent was observed with variability of 6.9 percent RSD. The bias observed for the replacement TIM870 was lower than on the existing TIM860, which reported biases of 19 percent for the 10 mg/L standard and 42 percent for the 5 mg/L standard. This high bias is expected for samples with alkalinities below 20 mg/L when using the endpoint titration method. It is always more accurate to measure alkalinity in the field. In addition, an inflection point method should be used for samples with alkalinities below 20 mg/L as $CaCO_3$ (Eaton and others, 1998). In Fiscal Year 2014, 8 percent of the alkalinity samples analyzed at the NWQL were above the detection limit and below 20 mg/L, but in Fiscal Year 2015 only 4 percent of samples analyzed were in this range.

Table 4. Alkalinity of known standards and a standard reference sample for estimates of bias and variability.

[ANC, acid-neutralizing capacity; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; TIM860, existing automated titration instrument; TIM870, replacement automated titration instrument; %, percent; RSD, relative standard deviation]

	Repeated alkalinity and ANC measurements (mg/L as $CaCO_3$)									
	10 mg/L standard		100 mg/L standard		500 mg/L standard		Standard reference sample		Third-party check	
	TIM860	TIM870	TIM860	TIM870	TIM860	TIM870	TIM860	TIM870	TIM860	TIM870
	11.82	11.92	100.7	99.12	502.1	496.5	30.47	30.67	36.06	35.74
	12.19	11.86	100.8	100	502.2	490.4	30.56	30.65	36.10	35.99
	12.03	11.46	100.7	99.59	502.5	491.7	30.57	30.26	36.13	35.54
	11.92	11.48	101.0	99.79	502.6	497.0	30.59	30.42	36.69	38.48
	11.86	11.48	100.8	99.24	503.5	498.9	30.66	30.37	36.70	37.98
	11.87	11.83	100.7	99.67	503.2	500.2	30.55	30.27	36.71	37.05
	11.93	11.43	103.9	103.7	503.2	493.8	30.47	30.53	36.77	37.88
			104.1	102.7	502.3	496.2	30.50	30.49	36.67	36.04
					503.0	501.1			36.78	36.13
					512.1	507.2			36.61	36.53
					512.1	505.3			36.67	36.09
									36.73	36.54
									37.24	38.61
Calculated mean	11.95	11.64	101.6	100.5	504.4	498.0	30.55	30.46	36.60	36.82
Expected alkalinity	10	10	100	100	500	500	29.6	29.6	36.45	36.45
Standard deviation	0.127	0.220	1.493	1.725	3.816	5.242	0.065	0.157	0.328	1.071
% RSD	1.062	1.891	1.470	1.717	0.756	1.053	0.212	0.514	0.896	2.908
Mean % recovery	119.5	116.4	101.6	100.5	100.9	99.6	103.2	102.9	100.4	101.0

Table 5. Alkalinity and acid-neutralizing capacity (ANC) measurements of various, blended groundwaters and surface waters for the determination of instrument variability.

[ANC, acid-neutralizing capacity; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; TIM860, existing automated titration instrument; TIM870, replacement automated titration instrument; %, percent; RSD, relative standard deviation; Mean % difference, mean percent difference equals (TIM870 minus TIM860) divided by TIM860 times 100]

	Alkalinity and ANC measurements (mg/L as $CaCO_3$)[1]							
	Low alkalinity[2] groundwater		Low alkalinity[2] surface water		High alkalinity[2] groundwater		High alkalinity[2] surface water	
	TIM860	TIM870	TIM860	TIM870	TIM860	TIM870	TIM860	TIM870
	26.36	26.34	8.643	8.832	194.2	190.4	425.7	417.2
	26.40	26.42	8.673	8.974	194.4	188.4	426.2	421.2
	26.42	26.34	8.691	8.207	195.0	191.5	427.0	427.6
	26.44	26.16	8.713	8.12	195.0	191.1	427.1	425.7
	26.49	25.90	8.728	8.242	195.1	192.0	427.3	424.6
	26.42	26.21	8.768	8.171	191.7	187.7		
Calculated mean	26.42	26.22	8.703	8.424	194.2	190.2	426.7	423.3
Standard deviation	0.043	0.187	0.044	0.376	1.294	1.747	0.680	4.110
RSD	0.163	0.712	0.503	4.459	0.666	0.919	0.159	0.971
Mean % difference	–0.757		–3.206		–2.060		–0.797	

[1]*Note:* Alkalinity and ANC are the same measurement. However, alkalinity is performed on a filtered sample while ANC uses an unfiltered sample.

[2]"Low alkalinity" samples are defined as samples with alkalinity or ANC concentrations less than one-third of the alkalinity and ANC concentration range of samples (groundwater or surface water) analyzed at the National Water Quality Laboratory (NWQL) 2014–2015. "High alkalinity" samples are defined as samples that have concentrations greater than two-thirds the range of sample concentrations for samples (groundwater or surface water) analyzed at the NWQL 2014–2015.

In addition to the four certified reference material standards, an assessment of alkalinity bias and precision was performed using a third party known standard and a standard reference sample. Excellent performance was observed for these measurements (table 4). Thirteen aliquots of the third party alkalinity standard were analyzed and demonstrated a 1 percent positive bias that were well within the limits to which data are reported. All demonstrated excellent reproducibility, with a 2.9 percent RSD. A standard reference sample from the U.S. Geological Survey Branch of Quality Systems was analyzed eight times, with a positive bias of 2.9 percent. It showed excellent reproducibility, with a RSD of 0.5 percent.

3.3 Variability of repeated alkalinity and acid-neutralizing capacity (ANC) measurements of groundwater and surface waters

Analyses of alkalinity and ANC data on blended, unfiltered groundwater and surface waters were performed (table 5). For the low alkalinity groundwater, low variability was shown with an RSD of 0.71 percent. For the high alkalinity groundwater, the RSD was 0.92 percent. The surface water samples also had low variability. The low alkalinity surface water had an RSD of 4.5 percent. The high alkalinity surface water had an RSD of 0.97 percent.

3.4 Comparison data from environmental samples

Seventy-five environmental samples were analyzed on both titration instruments, consisting of 52 alkalinity samples and 23 ANC samples. For alkalinity (LC 2109) and ANC (LC 70), the titration method is the same. The only difference is the bottle type, filtered and unfiltered, respectively. Since the data were analyzed separately, but showed no difference between the laboratory codes, the data are presented together below to show the reproducibility between the existing and replacement instruments. The mean percent difference between instruments for alkalinity samples was –1.7 percent, and the mean percent difference for ANC samples was –0.79 percent. The mean percent difference for all samples run was –1.4 percent. Excellent comparability between the two instruments was observed for sample alkalinity and ANC measurements in the typical range of NWQL samples (figs. 1 and 2; attachment 1).

3.5 Blank measurements

Blank samples (ASTM Type 1 water) were run as quality control samples and also interspersed throughout runs (attachment 3). All blanks measured were well below the NWQL detection limit of 4.0 mg/L as $CaCO_3$. The blanks analyzed on the replacement TIM870 have a mean concentration that is 14 percent lower than the existing TIM860. A carryover experiment was conducted in which blanks were run after high alkalinity samples, and all blanks results were below detection limit (attachment 2).

4 SUMMARY

The replacement TIM870 instrument to measure alkalinity and acid-neutralizing capacity (ANC) demonstrates excellent bias and variability for both alkalinity and ANC at concentrations above 20 mg/L as $CaCO_3$. Low bias and variability were obtained for comparison samples in the typical alkalinity and ANC ranges. Water Science Centers should expect that sample results from the new instrument will have less than 2 percent differences in alkalinity and ANC when compared to historical results for these laboratory codes. The NWQL detection limits will remain the same for the replacement instrument and will be reassessed after the instrument has been in production for at least 1 year.

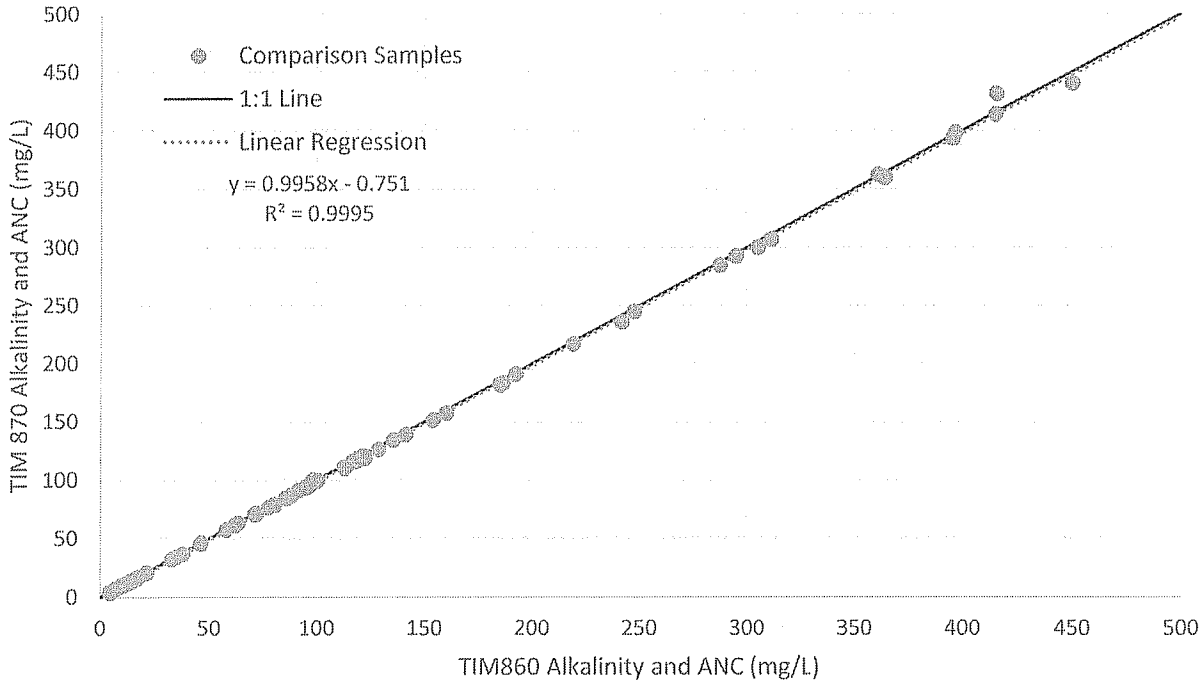

Figure 1. Alkalinity and acid-neutralizing capacity (ANC) measurements from environmental samples on the existing TIM860 instrument and the replacement TIM870 instrument (in mg/L as $CaCO_3$). Data are plotted over a 1:1 line.

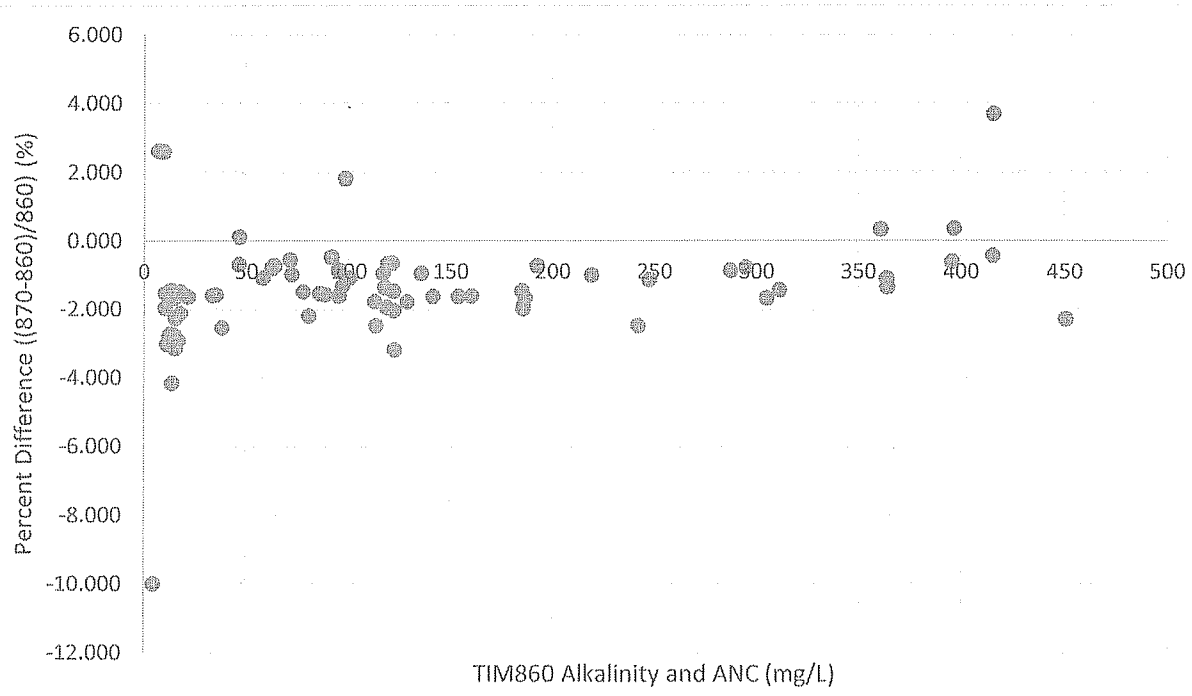

Figure 2. Percent difference of alkalinity and acid-neutralizing capacity (ANC) measurements between the existing TIM860 instrument and the replacement TIM870 instrument versus the alkalinity and ANC measured on the TIM860 (in mg/L $CaCO_3$).

5 LITERATURE CITED

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National Water Quality Laboratory SOP INCM0091.*x*, Determination of alkalinity and acid-neutralizing capacity automated electrometric titration *[Note: A copy of the unpublished NWQL standard operating procedure is available by request to labhelp@usgs.gov.]*

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6 ATTACHMENTS

Attachment 1 – Measured alkalinity and acid-neutralizing capacity (ANC) of environmental samples on both TIM860 (existing instrument) and TIM870 (replacement instrument), following National Water Quality Laboratory standard operating procedure INCM0091.7

Attachment 2 – Assessment of carryover for alkalinity and acid-neutralizing capacity (ANC) on TIM870 (replacement instrument) following National Water Quality Laboratory standard operating procedure INCM0091.7

Attachment 3 – Measured alkalinity and acid-neutralizing capacity (ANC) on blanks for both TIM860 (existing instrument) and TIM870 (replacement instrument)

Douglas L. Stevenson

/signed/
Douglas L. Stevenson, Acting Chief
National Water Quality Laboratory
Branch of Analytical Services

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Attachment 1

Measured alkalinity and acid-neutralizing capacity (ANC) of environmental samples on both TIM860 (existing instrument) and TIM870 (replacement instrument), following National Water Quality Laboratory standard operating procedure INCM0091.7

[ID, identification; % Dif, percent difference equals (measurement on TIM870 minus measurement on TIM860) divided by measurement on TIM860 times 100; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; –, minus]

Date and time	Sample ID	Laboratory code	TIM860	TIM870	Reporting unit	% Dif
1/20/2016 10:10:36 AM	20151980043	70	3.211	4.280	mg/L $CaCO_3$	33.292
2/5/2016 10:38:42 AM	20152080072	2109	2.371	1.800	mg/L $CaCO_3$	–24.083
2/2/2016 9:35:56 AM	20151970048	2109	4.428	3.985	mg/L $CaCO_3$	–10.005
1/20/2016 12:04:17 PM	20152050074	70	6.760	6.937	mg/L $CaCO_3$	2.618
1/20/2016 9:53:17 AM	20151960086	70	9.281	9.522	mg/L $CaCO_3$	2.597
2/2/2016 9:58:49 AM	20152710004	2109	10.20	10.00	mg/L $CaCO_3$	–1.961
2/2/2016 9:38:33 AM	20152520040	2109	10.33	10.17	mg/L $CaCO_3$	–1.549
2/5/2016 11:01:18 AM	20152100106	2109	10.91	10.58	mg/L $CaCO_3$	–3.025
2/5/2016 11:45:57 AM	20152150053	2109	12.04	11.70	mg/L $CaCO_3$	–2.824
2/5/2016 9:39:56 AM	20152030126	2109	12.47	12.13	mg/L $CaCO_3$	–2.727
2/5/2016 11:49:01 AM	20152150055	2109	13.04	12.85	mg/L $CaCO_3$	–1.457
2/5/2016 10:58:09 AM	20152100105	2109	13.44	12.88	mg/L $CaCO_3$	–4.167
2/2/2016 9:44:10 AM	20152460063	2109	14.21	13.97	mg/L $CaCO_3$	–1.689
2/2/2016 9:55:54 AM	20152540137	2109	14.46	14.06	mg/L $CaCO_3$	–2.766
2/2/2016 9:50:03 AM	20152540206	2109	14.93	14.46	mg/L $CaCO_3$	–3.148
2/2/2016 9:41:19 AM	20152520083	2109	15.02	14.68	mg/L $CaCO_3$	–2.264
2/2/2016 9:52:57 AM	20152540207	2109	16.49	16.01	mg/L $CaCO_3$	–2.911
2/2/2016 9:47:04 AM	20152540204	2109	17.43	17.06	mg/L $CaCO_3$	–2.123
2/2/2016 10:01:38 AM	20152580046	2109	17.46	17.20	mg/L $CaCO_3$	–1.489
1/6/2016 1:30:38 PM	20151970131	2109	21.36	21.01	mg/L $CaCO_3$	–1.639
1/6/2016 1:08:49 PM	20151970043	2109	33.09	32.56	mg/L $CaCO_3$	–1.602
1/20/2016 12:00:44 PM	20152050003	70	34.83	34.28	mg/L $CaCO_3$	–1.579
1/20/2016 11:53:24 AM	20152030074	70	37.72	36.76	mg/L $CaCO_3$	–2.545
1/20/2016 11:56:55 AM	20152050001	70	46.14	45.82	mg/L $CaCO_3$	–0.694
2/5/2016 9:07:42 AM	20151970136	2109	46.26	46.31	mg/L $CaCO_3$	0.108
1/6/2016 10:14:46 AM	20151250064	2109	57.96	57.33	mg/L $CaCO_3$	–1.087
1/20/2016 9:42:08 AM	20151260043	70	62.20	61.69	mg/L $CaCO_3$	–0.820
2/5/2016 9:35:39 AM	20152030091	2109	63.55	63.09	mg/L $CaCO_3$	–0.724
1/20/2016 10:48:57 AM	20151980209	70	71.23	70.83	mg/L $CaCO_3$	–0.562
1/6/2016 10:36:53 AM	20151270071	2109	71.94	71.23	mg/L $CaCO_3$	–0.987
1/6/2016 1:34:04 PM	20151970132	2109	77.55	76.39	mg/L $CaCO_3$	–1.496
1/6/2016 10:48:00 AM	20151270075	2109	80.39	78.62	mg/L $CaCO_3$	–2.202
2/5/2016 11:04:21 AM	20152110088	2109	85.56	84.24	mg/L $CaCO_3$	–1.543

Attachment 1

Measured alkalinity and acid-neutralizing capacity (ANC) of environmental samples on both TIM860 (existing instrument) and TIM870 (replacement instrument), following National Water Quality Laboratory standard operating procedure INCM0091.7—Continued

[ID, identification; % Dif, percent difference equals (measurement on TIM870 minus measurement on TIM860) divided by measurement on TIM860 times 100; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; –, minus]

Date (Time 860)	Sample ID	Laboratory code	TIM860	TIM870	Reporting unit	% Dif
1/20/2016 10:26:42 AM	20151980186	70	88.09	86.70	mg/L $CaCO_3$	–1.578
2/5/2016 10:53:01 AM	20152100066	2109	91.34	90.90	mg/L $CaCO_3$	–0.482
1/6/2016 10:24:06 AM	20151250164	2109	94.79	93.98	mg/L $CaCO_3$	–0.855
1/6/2016 10:09:38 AM	20151250061	2109	94.93	93.40	mg/L $CaCO_3$	–1.612
1/6/2016 10:18:56 AM	20151250067	2109	96.79	95.52	mg/L $CaCO_3$	–1.312
2/5/2016 9:18:29 AM	20152030061	2109	98.04	99.82	mg/L $CaCO_3$	1.816
1/20/2016 10:05:42 AM	20151980027	70	100.2	99.11	mg/L $CaCO_3$	–1.088
1/6/2016 12:55:23 PM	20151960079	2109	112.4	110.4	mg/L $CaCO_3$	–1.779
1/6/2016 12:49:30 PM	20151960078	2109	112.9	110.1	mg/L $CaCO_3$	–2.480
2/5/2016 11:29:09 AM	20152120169	2109	116.6	115.5	mg/L $CaCO_3$	–0.943
1/6/2016 12:43:37 PM	20151960076	2109	117.3	115.7	mg/L $CaCO_3$	–1.364
1/6/2016 12:31:40 PM	20151960071	2109	118.3	116.0	mg/L $CaCO_3$	–1.944
2/5/2016 9:29:45 AM	20152030066	2109	118.7	117.9	mg/L $CaCO_3$	–0.674
2/5/2016 9:23:47 AM	20152030064	2109	121.1	120.3	mg/L $CaCO_3$	–0.661
1/6/2016 12:37:36 PM	20151960072	2109	121.7	119.9	mg/L $CaCO_3$	–1.479
1/20/2016 10:13:06 AM	20151980124	70	121.8	119.3	mg/L $CaCO_3$	–2.053
1/20/2016 10:31:33 AM	20151980206	70	122.1	118.2	mg/L $CaCO_3$	–3.194
1/6/2016 11:23:49 AM	20151960069	2109	128.3	126.0	mg/L $CaCO_3$	–1.793
2/5/2016 10:32:27 AM	20152040062	2109	135.3	134.0	mg/L $CaCO_3$	–0.961
1/20/2016 10:42:48 AM	20151980208	70	141.1	138.8	mg/L $CaCO_3$	–1.630
1/6/2016 10:41:22 AM	20151270073	2109	153.7	151.2	mg/L $CaCO_3$	–1.627
2/5/2016 9:11:30 AM	20152020050	2109	160.0	157.4	mg/L $CaCO_3$	–1.625
1/6/2016 1:12:23 PM	20151970077	2109	184.7	182.0	mg/L $CaCO_3$	–1.462
1/6/2016 10:29:18 AM	20151270067	2109	185.1	181.4	mg/L $CaCO_3$	–1.999
1/6/2016 1:01:05 PM	20151970040	2109	185.4	181.8	mg/L $CaCO_3$	–1.942
2/5/2016 11:52:07 AM	20153030095	2109	186.2	183.1	mg/L $CaCO_3$	–1.665
1/20/2016 9:46:07 AM	20151260063	70	192.2	190.8	mg/L $CaCO_3$	–0.728
2/5/2016 11:09:20 AM	20152110159	2109	219.0	216.8	mg/L $CaCO_3$	–1.005
1/20/2016 10:18:29 AM	20151980173	70	241.8	235.8	mg/L $CaCO_3$	–2.481
2/5/2016 9:42:47 AM	20152030156	2109	247.5	244.7	mg/L $CaCO_3$	–1.131
1/6/2016 1:19:58 PM	20151970078	2109	287.1	284.6	mg/L $CaCO_3$	–0.871
2/5/2016 11:35:05 AM	20152120170	2109	294.7	292.4	mg/L $CaCO_3$	–0.780
1/20/2016 9:55:59 AM	20151970034	70	304.9	299.8	mg/L $CaCO_3$	–1.673
2/5/2016 11:17:59 AM	20152120167	2109	311.2	306.7	mg/L $CaCO_3$	–1.446

Attachment 1

Measured alkalinity and acid-neutralizing capacity (ANC) of environmental samples on both TIM860 (existing instrument) and TIM870 (replacement instrument), following National Water Quality Laboratory standard operating procedure INCM0091.7—Continued

[ID, identification; % Dif, percent difference equals (measurement on TIM870 minus measurement on TIM860) divided by measurement on TIM860 times 100; mg/L, milligram per liter; $CaCO_3$, calcium carbonate; –, minus]

Date (Time 860)	Sample ID	Laboratory code	TIM860	TIM870	Reporting unit	% Dif
1/6/2016 11:09:48 AM	20151950068	2109	360.9	362.1	mg/L $CaCO_3$	0.333
2/5/2016 10:04:34 AM	20152040021	2109	363.7	359.7	mg/L $CaCO_3$	–1.100
2/5/2016 9:52:00 AM	20152030157	2109	364.0	359.1	mg/L $CaCO_3$	–1.346
1/20/2016 12:07:05 PM	20152090005	70	395.5	393.1	mg/L $CaCO_3$	–0.607
1/6/2016 10:52:47 AM	20151950067	2109	396.6	398.0	mg/L $CaCO_3$	0.353
1/20/2016 12:25:41 PM	20152100124	70	415.3	413.5	mg/L $CaCO_3$	–0.433
1/20/2016 11:06:59 AM	20152020046	70	415.8	431.1	mg/L $CaCO_3$	3.680
1/20/2016 10:53:24 AM	20152020045	70	450.3	440.0	mg/L $CaCO_3$	–2.287
					Mean percent difference	**–1.427**

Attachment 2

Assessment of carryover for alkalinity and acid-neutralizing capacity (ANC) on TIM870 (replacement instrument) following National Water Quality Laboratory standard operating procedure INCM0091.7

[mg/L, milligram per liter; $CaCO_3$, calcium carbonate; TPC, third-party check; GSL, Great Salt Lake surface water]

Sample ID	Result (mg/L as $CaCO_3$)
BLANK	2.01
TPC	37.86
NaHCO3 #1	1081
BLANK	2.247
NaHCO3 #2	1087
BLANK	2.063
NaHCO3 #3	1080
BLANK	2.175
NaHCO3 #4	1088
BLANK	2.077
NaHCO3 #5	1081
BLANK	2.103
NaHCO3 #6	1092
BLANK	2.116
NaHCO3 #7	1086
BLANK	1.97
TPC	36.35
BLANK	1.792
TPC	35.72
BLANK	1.615
BLANK	1.601
BLANK	1.623
TPC	36.08
BLANK	1.812
NaHCO3 #1	1713
BLANK	1.711
NaHCO3 #2	1722
BLANK	1.932
NaHCO3 #3	1701
BLANK	1.959
TPC	36.57
GSL #1	179.4
BLANK	2.466
GSL #2	179.4
BLANK	2.353
TPC	37.07

Notes: Challenging samples (high alkalinity or specific conductance) were interspersed among blanks to assess carryover. All blank alkalinities are below the minimum report limit of 4.0 mg/L as $CaCO_3$ for alkalinity and for ANC. The TPC certified value = 36.45 mg/L as $CaCO_3$.

Attachment 3

Measured alkalinity and acid-neutralizing capacity (ANC) on blanks for both TIM860 (existing instrument) and TIM870 (replacement instrument)

[mg/L, milligram per liter; $CaCO_3$, calcium carbonate]

Sample ID	Measured alkalinity and acid-neutralizing capacity (mg/L as $CaCO_3$)	
	TIM860	TIM870
BLANK	2.318	2.173
BLANK	2.388	ϖ.522
BLANK	2.391	1.733
BLANK	2.404	2.040
BLANK	2.412	1.817
BLANK	2.434	1.641
BLANK	2.436	2.761
BLANK	2.368	1.591
BLANK	2.370	1.908
BLANK	2.195	1.626
BLANK	2.271	1.741
BLANK	2.314	1.819
BLANK	2.244	2.519
BLANK	2.344	2.263